

Simple Molecules and Clocks

S. Schiller

*Institut für Experimentalphysik, Heinrich-Heine-Universität
Düsseldorf, 40225 Düsseldorf, Germany*

D. Bakalov

*Institute for Nuclear Research and Nuclear Energy,
Tsarigradsko chaussée 72, Sofia 1784, Bulgaria*

V.I. Korobov

Joint Institute for Nuclear Research, 141980, Dubna, Russia

Abstract

The precise measurement of transition frequencies in cold, trapped molecules has applications in fundamental physics, and extremely high accuracies are desirable. We determine suitable candidates by considering simple molecules with a single electron, for which the external-field shift coefficients can be calculated with high precision. Our calculations show that H_2^+ exhibits particular transitions whose fractional uncertainties may reach 2×10^{-17} at room temperature. We also generalize the method of composite frequencies, introducing tailored linear combinations of individual transition frequencies that are free of the major systematic shifts, independent of the strength of the external perturbing fields. By applying this technique, the uncertainty should be reduced to the 10^{-18} range for both H_2^+ and HD^+ . Thus, the theoretical results demonstrate that these molecules are of metrological relevance for future studies.

Introduction

Frequency metrology of cold trapped molecules is an emerging field under intense development, driven by the promise of opening up new but challenging opportunities in fundamental physics. It has been proposed to use these systems to test the constancy of fundamental constants related to particle masses, by measuring vibrational transition frequencies over time or as a function of the gravitational potential [1]. Furthermore, the comparison of experimental molecular transition frequencies with ab-initio results can be used to test ab-initio theoretical calculations, in particular of QED effects [2, 3], to measure mass ratios of small nuclei, and to search for a fifth force on the sub-nanometer scale [4]. The search for parity violation effects on vibrational frequencies also requires extreme frequency accuracy [5]. A further potential application is a test of Lorentz Invariance, using oriented molecules [6]. Different molecular systems, diatomic and polyatomic, neutral and charged, are therefore being investigated [7–9].

Concerning the constancy of the electron-to-nuclear mass ratio, microwave cold atom clocks (exhibiting 2×10^{-16} fractional uncertainty) are already producing stringent limits. For molecules to become competitive systems, they must therefore have a potential uncertainty in the 10^{-17} range. A crucial aspect in molecular frequency metrology is thus the understanding of systematic frequency shifts in vibrational (or electronic) transitions, the development of methods allowing their suppression or, at least, their quantification, and the identification of candidate systems [10–15].

In this paper, we discuss and answer affirmatively the question whether it is in principle possible to reach extremely low inaccuracies (10^{-18} range) in the measurement of transition frequencies of molecules. Our scenario consists in considering *simple* molecules, i.e. molecules with one electron, for which the ab-initio theory has made significant advances in the last decade [16]. These allow not only the ab-initio calculation of transition frequencies with fractional inaccuracies of 4×10^{-11} , currently [17], but also the accurate calculation of the sensitivity to external fields, which is the focus here. Such ab-initio calculations were previously performed for a few simple *atomic* systems such as hydrogen and one-electron highly charged ions [18].

A significant difference between atomic and molecular system is that molecules have a multitude (many tens) of long-lived rovibrational levels in their electronic ground state, each of which may have a substantial number of hyperfine states. Thus, there is also a very large

number (e.g. thousands in molecular hydrogen ions) of transitions having high spectroscopic quality factors. Their external-field shift coefficients $\Delta\eta$ vary, often substantially, because the states' rovibrational molecular wave functions vary and as a consequence also the coefficients of the hyperfine Hamiltonian do. A subset of these transitions may exhibit small external-field shifts. The computability of the external-field shifts of simple molecules then has two main consequences. First, it permits selecting from this large set of transitions the metrologically most advantageous ones (i.e. having low sensitivity to external fields) based *entirely on theory*. Experimentally, one will apply the elegant techniques developed so far in the field of atomic ion clocks, for measuring and minimizing the various systematic shifts individually and estimating the residual uncertainty.

Second, the computability also enables a new approach for a reduction of the systematic shifts, which is particularly direct in molecules. Here, one performs, in fairly rapid succession, measurements of a set of N selected transitions with frequencies $\{f_1, f_2, \dots, f_N\}$ under time-constant and moderate, but otherwise arbitrary, external perturbations $\{X_j\}$, and numerically combines the results with weights β_i to a composite transition frequency $f_c = \sum_{i=1}^N \beta_i f_i$. For the studies mentioned above, such a composite frequency is as useful an observable as the frequency f_i of an individual transition.

Consider now that each individual frequency f_i is perturbed by the external fields present (magnetic field, electric field, electric field gradients, temperature, laser intensities, etc.) in a way expressible as a power series, $f_i(\{X_j\}) = f_{0,i} + \sum_j \Delta\eta_{j,i}(X_j)^{n_j}$, where $f_{0,i}$ are the unperturbed frequencies, and $\Delta\eta_{j,i}$ are the sensitivities to the external fields, given by the differences of the sensitivities (shift coefficients) of the final and initial states involved in the transition f_i , and calculable *ab-initio*. Only those contributions that are relevant for a desired accuracy of the composite frequency are included in the expansion, and the possible occurrence of different powers n_j for the same field X_j may also be taken into account.

The weights β_i are computed from the conditions that the sensitivities of the composite frequency to the external perturbations (up to the orders described by the above power expansion) vanish: $\partial f_c / \partial (X_j)^{n_j} = \sum_{i=1}^N \beta_i \Delta\eta_{j,i} = 0$. If M is the number of systematic effects to be canceled, including different algebraic dependencies on the perturbation strengths, there are M such equations, and one needs to measure at least $N = M + 1$ transitions, possibly having significantly different frequency, to satisfy them. Thus, the β_i are found by solving this set of equations; we stress that the β_i are functions of the theoretical shift coefficients

$\Delta\eta_{j,i}$, but are independent of the external fields. At a simpler level, composite frequencies are determined in atomic clocks, e.g. by averaging over several Zeeman components of the same (clock) hyperfine transition in order to suppress the linear Zeeman shift and electric quadrupole (EQ) shift [19].

Here we illustrate this concept for the one-electron molecules H_2^+ and HD^+ ; the extension to others, such as the other isotopologue molecular ions D_2^+ , \dots , is equally possible. Conceptually, we envision the spectroscopy of these ions to be performed on a single molecular ion, trapped in an ion trap. It is both sympathetically cooled to the Lamb-Dicke confinement regime, and interrogated by a laser-cooled atomic ion (Be^+) using a quantum-logic-type [20] or optical-force detection [21]. Techniques of quantum-state preparation are applied [3, 22, 23]. We consider here only one-photon transitions, which avoid the relatively large light shifts associated with the large intensities of the spectroscopy laser in two-photon transitions [15, 24]. In HD^+ the one-photon transitions are electric dipole (E1) transitions with quality factors of order 10^{13} ; in H_2^+ one has to resort to electric quadrupole (E2) transitions, since there are no allowed E1 transitions in the ground electronic state. Such transitions have been considered theoretically (without hyperfine structure effects) in Refs. [25, 26]. Since the lifetime of all H_2^+ levels exceeds 10^6 s, the transition quality factor will in practice be determined by the laser line width or the interrogation time. An electric quadrupole transition in a trapped and cooled molecular ion has recently been observed [27].

The systematic shifts and their calculation

The external field shifts relevant for a trapped molecular ion are the Zeeman shift, the Stark and EQ shift caused by the electric field of the ion trap, the black-body radiation (BBR) shift, light shifts and the 2nd-order Doppler shift. In this work, we treat explicitly the first four shifts. The light shift caused by the spectroscopy laser can be made negligible, as is known from research on atomic ion clocks that use E2 transitions. The 2nd-order Doppler shift scales inversely with the mass and thus will be significantly larger than in typical atomic ion clocks, at the fractional level 10^{-16} , and its uncertainty is therefore a relevant issue. While a discussion of the projected experimental level is beyond the scope of this work, nevertheless a value in the 10^{-18} range might be achievable.

We compute the systematic shifts by a combination of perturbation theory and direct diagonalization, limiting the spin basis states to those of a given level with vibrational and rotational quantum numbers v , L . Where necessary we use highly accurate non-adiabatic,

variational wave functions [28]. Because the hyperfine splitting and Zeeman shift typically dominate the other shifts, we first compute the eigenstates $|m(B)\rangle$ of the Hamiltonian $H_{\text{eff}}^{\text{hfs}}(v, L) + V^{\text{mag}}(v, L)$ [12, 29, 33, 36]. The states m are labeled with S , the (approximate) quantum number of the total spin, J , the total angular momentum, J_z , the projection on to the z -axis parallel to the magnetic field \mathbf{B} , and, for H_2^+ , I , the quantum number of the total nuclear spin, or, for HD^+ , F , the quantum number of the electron-proton coupled spin. For the Zeeman shift $E_Z(m(B))$, it is sufficient to consider the first two terms, $E_Z(m) \simeq \eta_B B + \eta_{B^2} B^2$ [12, 14]. For each eigenstate, we then compute the expectation value of the EQ and d.c. Stark effective interaction Hamiltonian, $V^{\text{EQ}}(v, L) + V^{\text{S}}(v, L)$, for given strengths of the additional external fields $X_j = V_{zz}, E_t, E_z$, where E_t (E_z) is the electric field component orthogonal (parallel) to \mathbf{B} and $V_{zz} = -\partial E_z / \partial z$. V^{EQ} and V^{S} have been derived in [15, 30] and only the results are given here. The EQ shift is, to a good approximation, $E_{\text{EQ}}(m) = \frac{3}{2} E_{14}(v, L) V_{zz} \langle m(B) | L_z^2 - \mathbf{L}^2 / 3 | m(B) \rangle$, where the quadrupole coefficients $E_{14}(v, L)$ have been computed in the Born-Oppenheimer (BO) approximation. The latter limits the fractional accuracy to $\simeq 10^{-3}$. Similarly, the Stark shift of an energy level is $E_S(m) = -[\alpha^{(t)}(m(B))(E_x^2 + E_y^2) + \alpha^{(l)}(m(B))E_z^2] / 2$, where the transverse and longitudinal polarisabilities are computed as $\alpha^{(t,l)}(m(B)) = \alpha_s(v, L) + \beta^{(t,l)} \alpha_t(v, L) \langle m(B) | L_z^2 - \mathbf{L}^2 / 3 | m(B) \rangle$, with $\beta^{(l)} = 2$, $\beta^{(t)} = -1$. Note that the same matrix element is involved in determining the dependency of the d.c. Stark and EQ shifts on the spin structure of a particular hyperfine state m . We have obtained the scalar ($\alpha_s(v, L)$) and tensor ($\alpha_t(v, L)$) polarisabilities non-adiabatically, using the non-relativistic variational wave functions, with inclusion of only electric interactions. Details will be reported elsewhere [30]. The inaccuracies of the polarisabilities stem from the neglect of relativistic corrections (of relative order α^2), and are therefore of order 10^{-4} fractionally.

The BBR shifts of a transition, Δf_{BB} , are determined by the dynamic polarisabilities, and for an isotropic (unpolarized) BBR field only the scalar parts $\alpha_s(\omega)$ for the initial and final states are relevant. The shift is to a very good approximation independent of the hyperfine state and only depends on the rovibrational levels (v, L) , (v', L') . With our extensive results on the polarisabilities and accurate transition dipoles [31] we computed the BBR shifts and their temperature derivatives for relevant transitions of HD^+ , extending the results of Ref. [13], and of H_2^+ . For the homonuclear ion H_2^+ the shift can be approximately obtained from the static scalar polarisability only, since its

E1 transitions have much higher frequencies than the typical BBR radiation frequencies, $\Delta f_{BB}(T_0) = \Delta \eta_T T_0^4 \simeq -(832 \text{ V/m})^2 (T_0/300 \text{ K})^4 \Delta \alpha_s / 2h$, where T_0 is the temperature of the BBR radiation field, and $\Delta \alpha_s = \alpha_s(v', L') - \alpha_s(v, L)$. We computed the correction of the shifts due to the frequency-dependence of the contribution of the excited electronic levels to the polarisability [30]. For H_2^+ we find it to be less than 1×10^{-3} fractionally for the transitions $v = 0, L = 1 \rightarrow v' < 4, L' = 1$ considered here. Here, it is sufficient to use the static approximation and thus the fractional inaccuracy of the BBR shift coefficients is $\sigma_{y, \Delta \eta_T} = 1 \times 10^{-3}$. For HD^+ , when taking into account all dynamic effects and neglect of relativistic corrections, we reach a theoretical absolute uncertainty of the level BBR shifts of 0.01 mHz. However, this uncertainty is so far available only for a few levels and we therefore conservatively assume an uncertainty $\sigma_{\text{abs}, \Delta f_{BB}} = 0.1 \text{ mHz}$.

Metrologically important transitions

We have performed the analysis of the systematic shifts of H_2^+ , which we have evaluated for a large number of levels. Our computations covered 26 states having v up to 8 and L up to 4. We have searched for metrologically advantageous transitions by first applying the criterion of particularly small Zeeman shifts. For experimental reasons it is reasonable to consider only transitions originating in the vibrational ground state $v = 0$ and we limited the final states to those for which $v' \leq 4$. We also note that the E2 transition strengths decrease rapidly with increasing $|v' - v|$ [25] and therefore small values are experimentally favorable. E2 transitions with small linear Zeeman shifts are the pairs between homologous hyperfine states, $I, S, J, J_z \rightarrow I' = I, S' = S, J' = J, J'_z = J_z$ having $S = I + 1/2$ when $I = 1$. Their small linear Zeeman shift $\Delta \eta_B$ is a result of the near-cancellation of the shifts η_B of lower and upper state, which each lie in the range $|\eta_B| \simeq (0.15 - 1.5) \text{ MHz/G}$ [33]. Importantly, their average Zeeman shift vanishes. A subset of favorable transitions is reported in Table I. It presents, among the transitions with $|\Delta \eta_B| < 10 \text{ Hz/G}$, the 15 having the smallest absolute electric quadrupole shifts.

The spectroscopy of a single hyperfine transition can already reach a high accuracy, for well-chosen transitions. We assume realistic experimental conditions and performance [34]. One technique for reducing some of the systematic shifts is based on noting that, as in atoms [19], the electric quadrupole shift and the tensor polarisability of a state are both proportional to $J(J+1) - 3J_z^2$ in weak magnetic fields. Therefore, both effects can be nulled by averaging over the $\Delta J_z = 0$ Zeeman components of a transition $J, J_z \rightarrow J' = J, J'_z =$

J_z , where J_z runs over all possible values $-J, \dots, J$. This approach is only applicable to the H_2^+ case, where all such transitions have small Zeeman shifts. The Zeeman shift is again nulled as well, because of the equal and opposite shifts of the transitions chosen above. The advantage compared to the orthogonal quantization technique is an expected higher suppression factor of the EQ shift and the additional nulling of the tensor Stark shift. Consider the 3.89 MHz hyperfine line of $(v = 0, L = 2) \rightarrow (v' = 1, L' = 2)$. We introduce the typical fractional time instability σ_{y,X_j} of the external perturbation X_j (i.e. B, E_z, E_t, V_{zz}) on the timescale of an individual transition frequency measurement, and assume $(\sigma_{y,B}, \sigma_{y,E}, \sigma_{y,V_{zz}}) = (1, 10, 5) \times 10^{-4}$. We obtain the Zeeman shift and EQ shift uncertainties $(\sigma_Z, \sigma_{EQ})/f = (4, 4) \times 10^{-18}$ and a negligible Stark shift uncertainty due to the field instability. The scalar Stark shift is not nulled, and its absolute value, 1.1×10^{-17} fractionally, is conservatively taken as Stark uncertainty σ_S/f . The fractional BBR shift is unchanged by the averaging and is $\Delta f_{BB}/f = -9.7 \times 10^{-17}$. While the theoretical uncertainty of this shift is negligible, the fractional uncertainty σ_{BB,T_0} associated with the experimental uncertainty σ_{T_0} of the BBR temperature is $\sigma_{BB,T_0}/f = 4(\sigma_{T_0}/T_0)|\Delta f_{BB}|/f \simeq 1.0 \times 10^{-17}$. The total uncertainty is $\sigma_{f,syst}/f = 1.6 \times 10^{-17}$, an outstandingly small value, similar to that of state-of-the art atomic ion clocks.

In HD^+ we recently determined that transitions with zero total angular momentum projection in the initial and final state, $J_z = 0 \rightarrow J'_z = 0$, are most favorable, since they exhibit a small quadratic Zeeman shift at low field [15]. We found no suitable transitions (within the reasonable requirement $v = 0, v' \leq 5$) having also particularly small electric quadrupole shift. We consider the $J_z = 0 \rightarrow J'_z = 0$ Zeeman component of the 71.1 MHz hyperfine line of the $(v = 0, L = 3) \rightarrow (5, 4)$ transition (261 THz), with particularly small quadratic Zeeman shift ($\Delta\eta_{B^2} = -2.3 \text{ Hz/G}^2$). Conservatively, we take the residual Zeeman and Stark shifts as uncertainties. Then the Zeeman, Stark and EQ shift uncertainties are $(\sigma_Z, \sigma_S, \sigma_{EQ})/f = (0.4, 1.7, 28) \times 10^{-17}$. The BBR shift is $\Delta f_{BB}/f = -1.8 \times 10^{-17}$, and its theoretical uncertainty $\sigma_{BB,\eta_T}/f = 2.6 \times 10^{-18}$. The experimental uncertainty due to σ_{T_0} is $\sigma_{BB,T_0}/f = 5 \times 10^{-19}$ [30]. We see that the EQ shift uncertainty dominates the total uncertainty, which at $\sigma_{f,syst}/f = 3 \times 10^{-16}$ is significantly higher than for H_2^+ .

The composite frequency method

We now exemplify the concept of composite frequency which allows reducing further the already small systematic shift uncertainties. A composite frequency $f_c = \sum_i \beta_i f_i$ is free

(v', L')	(v, L)	I'	S'	J'	J'_z	I	S	J	J_z	δf_0	$\Delta\eta_B$	$\Delta\eta_{V_{zz}}$	$\Delta\alpha^{(t)}$	$\Delta\alpha^{(l)}$	Δf_{BB}
upper	lower									[MHz]	[Hz/G]	[Hz m ² /GV]	[at. u.]	[at. u.]	[mHz]
(1, 1)	(0, 1)	1	$\frac{3}{2}$	$\frac{5}{2}$	$\pm\frac{3}{2}$	1	$\frac{3}{2}$	$\frac{5}{2}$	$\pm\frac{3}{2}$	-12.85	± 4.20	3.2	0.75	0.69	-6.3
(1, 2)	(0, 2)	0	$\frac{1}{2}$	$\frac{5}{2}$	$\pm\frac{3}{2}$	0	$\frac{1}{2}$	$\frac{5}{2}$	$\pm\frac{3}{2}$	-2.59	± 8.61	4.5	0.77	0.67	-6.4
(2, 1)	(0, 1)	1	$\frac{3}{2}$	$\frac{5}{2}$	$\pm\frac{3}{2}$	1	$\frac{3}{2}$	$\frac{5}{2}$	$\pm\frac{3}{2}$	-24.75	± 9.24	6.6	1.71	1.55	-14.3
(1, 1)	(0, 1)	1	$\frac{3}{2}$	$\frac{5}{2}$	$\pm\frac{1}{2}$	1	$\frac{3}{2}$	$\frac{5}{2}$	$\pm\frac{1}{2}$	-12.85	± 1.40	12.6	0.82	0.55	-6.3
(1, 3)	(0, 3)	1	$\frac{3}{2}$	$\frac{3}{2}$	$\pm\frac{1}{2}$	1	$\frac{3}{2}$	$\frac{3}{2}$	$\pm\frac{1}{2}$	-4.63	± 6.02	12.7	0.84	0.56	-6.4
(1, 3)	(0, 3)	1	$\frac{3}{2}$	$\frac{9}{2}$	$\pm\frac{3}{2}$	1	$\frac{3}{2}$	$\frac{9}{2}$	$\pm\frac{3}{2}$	-14.88	± 7.56	13.4	0.84	0.55	-6.4
(1, 4)	(0, 4)	0	$\frac{1}{2}$	$\frac{9}{2}$	$\pm\frac{3}{2}$	0	$\frac{1}{2}$	$\frac{9}{2}$	$\pm\frac{3}{2}$	-5.09	± 9.87	14.6	0.87	0.54	-6.5
(1, 1)	(0, 1)	1	$\frac{3}{2}$	$\frac{5}{2}$	$\pm\frac{5}{2}$	1	$\frac{3}{2}$	$\frac{5}{2}$	$\pm\frac{5}{2}$	-12.85	± 7.00	-15.7	0.62	0.96	-6.3
(1, 2)	(0, 2)	0	$\frac{1}{2}$	$\frac{3}{2}$	$\pm\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{3}{2}$	$\pm\frac{1}{2}$	3.89	± 4.27	15.9	0.85	0.51	-6.4
(1, 3)	(0, 3)	1	$\frac{3}{2}$	$\frac{9}{2}$	$\pm\frac{1}{2}$	1	$\frac{3}{2}$	$\frac{9}{2}$	$\pm\frac{1}{2}$	-14.88	± 2.52	17.7	0.88	0.49	-6.4
(1, 2)	(0, 2)	0	$\frac{1}{2}$	$\frac{5}{2}$	$\pm\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{5}{2}$	$\pm\frac{1}{2}$	-2.59	± 2.87	18.2	0.87	0.48	-6.4
(1, 4)	(0, 4)	0	$\frac{1}{2}$	$\frac{7}{2}$	$\pm\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{7}{2}$	$\pm\frac{1}{2}$	6.36	± 4.13	19.1	0.9	0.48	-6.5
(1, 4)	(0, 4)	0	$\frac{1}{2}$	$\frac{9}{2}$	$\pm\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{9}{2}$	$\pm\frac{1}{2}$	-5.09	± 3.29	19.5	0.9	0.47	-6.5
(2, 1)	(0, 1)	1	$\frac{3}{2}$	$\frac{5}{2}$	$\pm\frac{1}{2}$	1	$\frac{3}{2}$	$\frac{5}{2}$	$\pm\frac{1}{2}$	-24.75	± 3.08	26.2	1.87	1.23	-14.3
(2, 2)	(0, 2)	0	$\frac{1}{2}$	$\frac{3}{2}$	$\pm\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{3}{2}$	$\pm\frac{1}{2}$	7.60	± 9.24	33.0	1.94	1.14	-14.4

Table I: Systematic shifts of selected electric-quadrupole rovibrational transitions in H_2^+ , ordered according to the absolute value of electric quadrupole shift. The transitions are between the levels $m : (v = 0, L, I, S, J, J_z) \rightarrow m' : (v', L', I', S', J', J'_z)$ (lower \rightarrow upper). Note that several Zeeman components of the same hyperfine transition occur. δf_0 is the spin-dependent contribution to the total transition frequency f_0 , at 0 G. $\Delta\eta_B$ denotes the Zeeman shift coefficient of the transition frequency; $\Delta\eta_{V_{zz}}$ is the electric quadrupole shift coefficient at 0 G. $\Delta\alpha^{(t)} = \alpha^{(t)}(m') - \alpha^{(t)}(m)$, $\Delta\alpha^{(l)} = \alpha^{(l)}(m') - \alpha^{(l)}(m)$ are the transverse and longitudinal difference electric polarisabilities between upper (m') and lower state (m), respectively, in atomic units and in zero magnetic field. The two signs for J_z and J'_z indicate the transition pair $+\rightarrow +, -\rightarrow -$. Δf_{BB} is the BBR shift at $T_0 = 300$ K. For the $(0, 1) \rightarrow (1, 1)$ transition, the absolute frequency $f_0 \simeq 65.6$ THz, for the $(0, 1) \rightarrow (2, 1)$ transition, $f_0 \simeq 127$ THz.

of Zeeman, quadrupole and Stark shift if the four conditions $\sum_i \beta_i \Delta \eta_{B,i} = 0$ (pure linear Zeeman effect for particular transitions of H_2^+), $\sum_i \beta_i \Delta \eta_{B^2,i} = 0$ (pure quadratic Zeeman effect for particular transitions of HD^+), $\sum_i \beta_i \Delta \eta_{V_{zz},i} = 0$, $\sum_i \beta_i \Delta \alpha_i^{(l)} = 0$, $\sum_i \beta_i \Delta \alpha_i^{(t)} = 0$ are satisfied, respectively, assuming that the potential individual transitions are selected as described above. For the homonuclear molecular hydrogen ions, the latter two conditions also eliminate the “composite” scalar polarisability and thus eliminate the (static) BBR shift, independently of the temperature T_0 , since all individual shifts are proportional to T_0^4 in the static approximation. For HD^+ there is no such simple dependence [30], and the BBR shift cancellation constraint, for a particular temperature T_0 , is $\sum_i \beta_i \Delta f_{BB,i}(T_0) = 0$, and represents a fifth condition.

If we choose $N = 5$ transitions for H_2^+ or $N = 6$ for HD^+ we find a corresponding solution $\{\beta_i\}$ (up to a common factor). But since there exists a large number ($\gg N$) of transitions with weak systematic shifts that may be employed, a large number K of solutions $\{\beta_i\}_K$ exists, with a corresponding transition set $\{i_1, \dots, i_N\}_K$ for each. We may therefore further down-select the solutions according to additional criteria. Obviously, the accuracy of cancellation of the shifts depends on the inaccuracies of the theoretical shift coefficients σ_{y,η_j} (which as shown above are low and will be reduced further with future theory work) and on the amount of variation σ_{y,X_j} of the perturbations in-between measurements of individual frequencies (which is to be minimized experimentally). We can then compute, for each solution, the total absolute uncertainty $\sigma_{f_c, \text{synt}}$ of the composite frequency as $\sigma_{f_c, \text{synt}}^2 = \sum_j \sigma_j^2 = \sum_{i,j} (\sigma_{y,\Delta \eta_{j,i}}^2 + \sigma_{y,X_j}^2 n_j^2) \beta_i^2 (\Delta \eta_{j,i} X_j^{n_j})^2$ and select a solution with a low value. Note that for given $\{\sigma_{y,\Delta \eta_{j,i}}\}$, $\{\sigma_{y,X_j}\}$ and a desired level of $\sigma_{f_c, \text{synt}}$ this leads to conditions for the maximum permitted strengths of the external fields X_j .

We have performed a numerical search for the composite frequency with lowest fractional systematic uncertainty $\sigma_{f_c, \text{synt}}/f_c$. We find that there are many solutions with very close values. Table II gives one example for each ion.

For H_2^+ we have considered, in order to show the essence of the method, the scenario where not all $J_z \rightarrow J'_z = J_z$ components of each hyperfine transition are measured, as in the example above, but instead the minimum number $N = 5$ of transitions that enables canceling the $M = 4$ systematic effects. In addition, the static BBR shift is canceled “for free”. The solution shown was chosen to include only two values of v' , reducing the number of required lasers to only two. The uncertainties of the scalar Stark shift and of the BBR shift

Table II: Examples of composite frequencies f_c and the contributing individual transitions. Top: HD^+ ; bottom: H_2^+ . The uncertainties of the BBR shifts of the individual transitions due to the BBR temperature uncertainty σ_{T_0} , $\sigma_{BB,T_0} = \sigma_{T_0} |d\Delta f_{BB}(T_0)/dT_0|$ are listed; however, for both ions the corresponding uncertainty of the composite BBR shift $\Delta f_{BB,f_c}$ is negligible. Δf_Z is the Zeeman shift in 1 G. σ_Z , $\sigma_{S,\text{transv}}$, $\sigma_{S,\text{long}}$, σ_{EQ} , σ_{BB} are the uncertainties of f_c due to field instabilities and theoretical shift coefficient uncertainties for, respectively, the Zeeman, Stark (transv.), Stark (long.), EQ, and BBR effect. For H_2^+ , $B = 0.1$ G, $V_{zz} = 0.67 \times 10^8$ V/m², $\sigma_{y,B} = 1 \times 10^{-4}$, $\sigma_{y,\eta_B,i} = 0.1 \times 10^{-4}$, $\sigma_{y,\eta_T,i} = 1 \times 10^{-3}$. For HD^+ , $B = 0.02$ G, $V_{zz} = 0.2 \times 10^8$ V/m², $\sigma_{y,B} = 10 \times 10^{-4}$, $\sigma_{y,\eta_B,i} = 1 \times 10^{-4}$, $\sigma_{\text{abs},\eta_T,i} = 0.1$ mHz. Common parameters: $T_0 = 300$ K, $\sigma_{T_0} = 8$ K, $(\sigma_{y,E}, \sigma_{y,V_{zz}}, \sigma_{y,T_{BBR}}) = (10, 1, 5) \times 10^{-4}$, $(\sigma_{y,\eta_E,i}, \sigma_{y,\eta_{V_{zz}},i}) = (3, 1) \times 10^{-4}$. The assumed uncertainty of the EQ shift coefficient $\sigma_{y,\eta_{V_{zz}},i}$ is 10 times smaller than available from our calculations [15], but will be obtainable by using variational rather than BO wavefunctions. Alternatively, V_{zz} may be reduced by a factor 10. Note the different values for V_{zz} assumed in the calculation of the uncertainties for H_2^+ and HD^+ ; however, for clarity of comparison, Δf_{EQ} in these tables is for a different, nominal value $V_{zz,\text{ref}} = 10^8$ V/m², for both ions.

HD ⁺	$f_c = 54.04 \text{ THz}, \sigma_{f_c, \text{syst}}/f_c = 5.1 \times 10^{-18}, \Delta f_{\text{BB}, f_c}/f_c = 3.2 \times 10^{-17}$ $(\sigma_Z, \sigma_{S, \text{transv}}, \sigma_{S, \text{long}}, \sigma_{\text{EQ}}, \sigma_{\text{BB}}) = (1.1, 0.1, 0.2, 3.9, 3.1) \times 10^{-18}$																
(v', L')	(v, L)	F'	S'	J'	J'_z	F	S	J	J_z	δf_0	Δf_Z	Δf_{EQ}	$\Delta \alpha^{(t)}$	$\Delta \alpha^{(l)}$	Δf_{BB}	σ_{BB, T_0}	ξ_i
upper	lower	upper				lower				[MHz]	[Hz]	[Hz]	[at. u.]	[at. u.]	[mHz]	[mHz]	
(1, 5)	(0, 4)	1	2	5	0	1	2	4	0	−3.1	−57.3	−3.5	0.4	1.6	−9.1	0.7	1
(2, 4)	(0, 3)	0	1	5	0	0	1	4	0	30.7	31.7	−4.0	−0.5	6.0	−13.1	1.2	−0.64
(2, 5)	(0, 4)	0	1	5	0	0	1	4	0	32.0	−38.9	−4.4	1.1	2.8	−13.5	1.3	−0.75
(2, 5)	(0, 4)	0	1	6	0	0	1	5	0	31.2	−39.6	−4.0	0.9	3.4	−13.5	1.3	−0.70
(3, 2)	(0, 1)	1	1	3	0	1	1	2	0	−3.8	21.2	−7.1	−20.8	49.6	−17.3	1.8	0.13
(5, 5)	(0, 4)	0	1	4	0	0	1	3	0	70.8	45.9	−10.8	8.3	1.4	−37.3	4.1	0.40

H ₂ ⁺	$f_c = 417.14 \text{ THz}, \sigma_{f_c, \text{syst}}/f_c = 3.8 \times 10^{-18}, \Delta f_{\text{BB}, f_c}/f_c = 0$ $(\sigma_Z, \sigma_{S, \text{transv}}, \sigma_{S, \text{long}}, \sigma_{\text{EQ}}, \sigma_{\text{BB}}) = (2.7, 0.1, 0., 2.4, 0.9) \times 10^{-18}$																
(v', L')	(v, L)	I'	S'	J'	J'_z	I	S	J	J_z	δf_0	Δf_Z	Δf_{EQ}	$\Delta \alpha^{(t)}$	$\Delta \alpha^{(l)}$	Δf_{BB}	σ_{BB, T_0}	ξ_i
upper	lower	upper				lower				[MHz]	[Hz]	[Hz]	[at. u.]	[at. u.]	[mHz]	[mHz]	
(3, 1)	(0, 1)	1	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{5}{2}$	1	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{5}{2}$	−35.77	23.09	−5.11	2.38	3.8	−24.6	2.6	1
(3, 1)	(0, 1)	1	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	1	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	−35.77	13.86	1.02	2.95	2.7	−24.6	2.6	4.95
(1, 1)	(0, 1)	1	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	1	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	−12.85	4.20	0.31	0.75	0.7	−6.3	0.7	−19.18
(1, 1)	(0, 1)	1	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{5}{2}$	1	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{5}{2}$	−12.85	7.00	−1.58	0.62	1.0	−6.3	0.7	−3.33
(1, 3)	(0, 3)	1	$\frac{3}{2}$	$\frac{3}{2}$	− $\frac{3}{2}$	1	$\frac{3}{2}$	$\frac{3}{2}$	− $\frac{3}{2}$	−4.63	−18.06	−1.27	0.65	0.9	−6.4	0.7	−0.67

are now significantly reduced compared to a single transition. In order to reduce the Zeeman shift uncertainty, first, the Zeeman coefficient uncertainty σ_{y,η_B} is assumed very small, 10^{-5} , which implies that relativistic contributions need to be computed, which is feasible [35]. Second, a small magnetic field $B = 0.1$ G is chosen. This value is still compatible with resolving individual Zeeman components, provided appropriate ultra-narrow-linewidth lasers are employed. The BBR shift uncertainty is due to the static approximation of the shift coefficients. In the total uncertainty, $\sigma_{f_c, \text{sys}}/f_c = 4 \times 10^{-18}$, the Zeeman and EQ shift uncertainties are now the dominant ones.

In the case of HD^+ , we show a particular solution where not the BBR shift but its derivative with respect to temperature is canceled, via the constraint $\sum_i \beta_i d\Delta f_{BB,i}(T_0)/dT_0 = 0$. We set again $B = 0.02$ G but can relax the requirement for magnetic field stability $\sigma_{y,B}$ compared to the H_2^+ case. This results in a composite BBR shift $\Delta f_{BB,f_c} = 3 \times 10^{-17}$. Its uncertainty $\sigma_{BB,\Delta\eta_T}/f_c = 3 \times 10^{-18}$ is dominated by the theoretical uncertainties of the individual BBR shifts. (As described above, this contribution will be reduced with future theory work.) We find a total uncertainty $\sigma_{f_c, \text{sys}}/f_c = 5 \times 10^{-18}$, limited in similar parts by the uncertainty of the EQ shift and of the BBR shift. Alternatively, we can choose to cancel the BBR shift instead of its derivative, but find that the best solutions yield a 20% larger total uncertainty.

Extension of the method

With the proposed approach, additional systematic shifts can in principle be compensated, as long as they are transition-dependent. Generally, the introduction of additional conditions will require inclusion of the same number of additional transitions in the composite frequency, but in some cases, the multitude of solutions canceling M shift types allows selecting one that minimizes one additional shift type. Compensation is possible, for example, of the light shift caused by the UV laser that cools the atomic ion, and whose light field may overlap with the molecular ion. Along the same line, the small corrections of the Zeeman shift contributions of higher order in B may be eliminated, which may be relevant when the applied magnetic field is not small enough. For H_2^+ this is the quadratic contribution $\Delta\eta_{B^2}B^2$, and for HD^+ , $\Delta\eta_{B^3}B^3$, where the coefficients are computable [12]. Therefore, the conditions $\sum_i \beta_i \Delta\eta_{B^2,i} = 0$, or $\sum_i \beta_i \Delta\eta_{B^3,i} = 0$ can be added.

In conclusion, we computed the external-field shift coefficients of the one-electron molecular ions H_2^+ and HD^+ , and have identified vibrational transitions in H_2^+ having extremely low

systematic shifts ($< 2 \times 10^{-17}$). Moreover, we have proposed to measure composite transition frequencies (selected by theoretical calculation) that are free of external-field shifts and should enable a systematic uncertainty as low as several 10^{-18} . The statistical uncertainty of the individually measured transition frequencies would then be a significant contribution to the total uncertainty, especially in the case of heteronuclear molecules, whose natural transition Q-factors are limited to 10^{13} . The expense of the composite frequency method is the need of performing spectroscopy and frequency measurements of $M + 1$ transitions (M being the number of systematic effects to be canceled), in different wavelength ranges. However, this is technologically feasible, as has been already shown in the case of HD^+ [2, 3]. Thus, our theoretical analysis provides a strong motivation and guide to future experiments employing molecules to probe fundamental physics issues.

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- [1] S. Schiller and V.I. Korobov, Phys. Rev. A **71**, 032505 (2005).
 - [2] J.C.J. Koelemeij, B. Roth, A. Wicht, I. Ernsting, S. Schiller, Phys. Rev. Lett. **98**, 173002 (2007).
 - [3] U. Bressel, A. Borodin, J. Shen, M. Hansen, I. Ernsting, S. Schiller, Phys. Rev. Lett. **108**, 183003 (2012)
 - [4] E. J. Salumbides, J. C. J. Koelemeij, J. Komasa, K. Pachucki, K. S. E. Eikema, W. Ubachs, Phys. Rev. D **87**, 112008 (2013); E. J. Salumbides, W. Ubachs, V. I. Korobov, arXiv:1308.1711, to appear in J. Molec. Spectr. (2013)
 - [5] S. K. Tokunaga, C. Stoeffler, F. Auguste, A. Shelkovnikov, C. Daussy, A. Amy-Klein, C. Chardonnet, B. Darquie, Mol. Phys. **111**, 2363–2373 (2013). doi:10.1080/00268976.2013.821186.
 - [6] H. Müller, S. Herrmann, A. Saenz, A. Peters, C. Lämmerzahl, Phys. Rev. D **70**, 076004 (2004).
 - [7] S. T. Kotochigova, T. Zelevinsky, J. Ye, Phys. Rev. A **79**, 012504 (2009). doi:10.1103/PhysRevA.79.012504.

- [8] G. Reinaudi, C. B. Osborn, M. McDonald, S. Kotochigova, T. Zelevinsky, *Phys. Rev. Lett.* **109**, 115303 (2012). doi:10.1103/PhysRevLett.109.115303
- [9] J. P. Karr, A. Douillet, L. Hilico, *Appl. Phys. B* **107**, 1043–1052 (2012); DOI 10.1007/s00340-011-4757-z
- [10] M. Kajita, G. Gopakumar, M. Abe, M. Hada, *Physical Review A* **85**, 062519 (2012). doi:10.1103/PhysRevA.85.062519.
- [11] M. Kajita, A. Minori, *J. Phys. B-At. Mol. and Opt. Phys.* **45**, 185401 (2012). doi:10.1088/0953-4075/45/18/185401.
- [12] D. Bakalov, V.I. Korobov, S. Schiller, *J. Phys. B: At. Mol. Opt. Phys.* **44**, 025003 (2011); Corrigendum: *J. Phys. B: At. Mol. Opt. Phys.* **45**, 049501 (2012).
- [13] J.C.J. Koelemeij, *Phys. Chem. Chem. Phys.* **13**, 18844 (2011).
- [14] D. Bakalov and S. Schiller, *Hyperfine Interact.* **210**, 25 (2012)
- [15] D. Bakalov and S. Schiller, *Appl. Phys. B* (2013). DOI 10.1007/s00340-013-5703-z and corrigendum, to appear
- [16] V. I. Korobov and Z.-X.Zhong, *Phys. Rev. A* **86**, 044501 (2012)
- [17] V. I. Korobov, L. Hilico, J. P. Karr, arXiv:1312.3728 [physics] (2013). <http://arxiv.org/abs/1312.3728>.
- [18] see references in: S. Schiller, *Phys. Rev. Lett.* **98**, 180801 (2007). doi:10.1103/PhysRevLett.98.180801.
- [19] P. Dube, A. A. Madej, J. E. Bernard, L. Marmet, J. S. Boulanger, S. Cundy, *Phys. Rev. Lett.* **95**, 033001 (2005). doi:10.1103/PhysRevLett.95.033001.
- [20] P. O. Schmidt, T. Rosenband, C. Langer, W. M. Itano, J. C. Bergquist, D. J. Wineland, *Science* **309**, 749–752 (2005). doi:10.1126/science.1114375
- [21] J.C.J. Koelemeij, B. Roth, S. Schiller, *Phys. Rev. A* **76**, 023413 (2007)
- [22] T. Schneider, B. Roth, H. Duncker, I. Ernsting, S. Schiller, *Nature Phys.* **6**, 275–278 (2010). doi:10.1038/NPHYS1605
- [23] P.F. Sta anum, K. Højbjerg, P. S. Skyt, A. K. Hansen, M. Drewsen, *Nature Phys.* **6**, 271–274. (2010). doi:10.1038/nphys1604.
- [24] J. P. Karr, S. Kilic, and L. Hilico, *J. Phys. B: At. Mol. Opt. Phys.* **38**, 853 (2005).
- [25] A. Posen, A. Dalgarno, J. Peek, *At. Data Nucl. Data Tables* **28**, 265 (1983)
- [26] H. Olivares Pilon and D. Baye, *J. Phys. B: At. Mol. Opt. Phys.* **45**, 065101 (2012);

- [27] S. Willitsch et al., 2nd IOTA COST Workshop on Cold Molecular Ions, Arosa, 2 - 5 September 2013
- [28] V.I. Korobov, D. Bakalov, H.J. Monkhorst, Phys. Rev. A **59**, R919 (1999).
- [29] V.I. Korobov, L. Hilico, and J. P. Karr, Phys. Rev. A **74**, 040502(R) (2006).
- [30] S. Schiller, V. Korobov, A. Bekabaev et al., in preparation.
- [31] Q.-L. Tian, L.-Y. Tang, Z.-X. Zhong, Z.-C. Yan, T.-Y. Shi, J. of Chem. Phys. **137**, 024311 (2012). doi:10.1063/1.4733988.
- [32] H. Olivares Pilón and D. Baye, J. Phys. B: At. Mol. Opt. Phys. **45**, 235101 (2012); <http://iopscience.iop.org/0953-4075/45/23/235101>, and H. Olivares Pilón, priv. comm.
- [33] J. P. Karr, V.I. Korobov, L. Hilico, Phys. Rev. A **77**, 062507 (2008)
- [34] Assumptions are: (i) H_2^+ : $B = 0.5$ G (chosen so as to allow spectral separation of the Zeeman components); HD^+ : $B = 0.02$ G; (ii) electric field gradient $V_{zz} = 0.67 \times 10^8$ V/m². Note that V_{zz} is determined by the trap endcap voltage and the axial potential curvature and both are large since the molecular ion and the atomic ion must be close in order to apply the quantum logic technique. For HD^+ : averaging the transition over three orthogonal quantization directions [15], and achieving a reduction of the EQ shift by a factor 100; (iii) residual, uncalibrated trap fields $E_z^2 = E_t^2 = (200 \text{ V/m})^2$. The corresponding Stark shift is taken as uncertainty; (iv) blackbody environment temperature $T_0 = 300$ K; Its uncertainty is assumed as $\sigma_{T_0} = 8$ K.
- [35] V. I. Korobov, Phys. Rev. A **63**, 044501 (2001)
- [36] D. Bakalov, V.I. Korobov, S. Schiller, Phys. Rev. Lett. **97**, 243001 (2006).